

The System Lime-Water at 21° C and High Pressures

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Compression measurements on the binary system $\text{Ca}(\text{OH})_2\text{-H}_2\text{O}$ at 21° C and high pressures show a large discontinuity in volume at 2,800 atmospheres which involves both components. Evidence is presented that the transition is the result of formation of a hydrate of lime, $\text{Ca}(\text{OH})_{2+n}\text{H}_2\text{O}$, where $4 \leq n \leq 6$. A pressure composition diagram for the system $\text{Ca}(\text{OH})_2\text{-H}_2\text{O}$ at 21° C is given.

1. Introduction

In a recent study of the properties of portland cements subjected to high hydrostatic pressure, a large volume discontinuity was noted in systems containing cement and free water [1].¹ By elimination procedures it was finally concluded that the volume discontinuity arose from the system $\text{Ca}(\text{OH})_2\text{-H}_2\text{O}$. The present report describes the results of direct studies on the system $\text{Ca}(\text{OH})_2\text{-H}_2\text{O}$ at 21° C and high pressures.

The literature on hydrate formation in alkaline earth hydroxides is extensive and will not be reviewed here. It is sufficient to note that although numerous reports have been made of hydrates of $\text{Ca}(\text{OH})_2$ at room temperature, none appear to be accepted as reliable [2] and no hydrate of $\text{Ca}(\text{OH})_2$ is believed to exist. As a result of the present studies it is concluded that a hydrate of $\text{Ca}(\text{OH})_2$ is stable at pressures above 3,000 atm at 21° C, and a rough pressure-composition diagram is proposed.

2. Experimental Method

Techniques and apparatus used here for studies of compression at high pressures have been described in detail [3]. Briefly, an experiment consists in forcing a leakproof piston into the bore of a heavy-walled pressure vessel that contains the specimen immersed in a light petroleum distillate (Varsol). Measurements are made of the depth of penetration of the piston at each 1,000 atm, the pressure being determined by means of a calibrated manganin pressure gage immersed in the Varsol inside the pressure vessel. Another experiment performed with a steel bar of comparable volume replacing the specimen permits calculation of the compression of the specimen in terms of that of steel, which is known.

The specimens used in these studies were mixtures of powdered $\text{Ca}(\text{OH})_2$ and distilled water contained in a cylindrical steel tube open to the confining liquid at one end. $\text{Ca}(\text{OH})_2$ was of chemical reagent grade and was weighed out in the tube. Freshly distilled water was also weighed into the tube, so that the weights of both components were known. Each water- $\text{Ca}(\text{OH})_2$ mixture was stirred thoroughly

to obtain a uniform mixture and then stirred with Varsol prior to compression. The dry $\text{Ca}(\text{OH})_2$ was treated in a similar manner except that no water was added. Following compression of this specimen, the volume was determined by hydrostatic weighing in Varsol. The resulting calculated density for the $\text{Ca}(\text{OH})_2$ was used to calculate the volumes of $\text{Ca}(\text{OH})_2$ in all experiments in which water- $\text{Ca}(\text{OH})_2$ mixtures were used. The volume of the water was calculated from known data for the density of water. The amount of $\text{Ca}(\text{OH})_2$ dissolved was neglected in this calculation.

3. Results and Discussion

The results of compression measurements on the various mixtures are given in table 1. The mole fraction of $\text{Ca}(\text{OH})_2$ in each mixture is tabulated at the head of each corresponding column of compression data. The compressions are expressed in terms of $-\Delta V/V_0$, where $-\Delta V$ is reckoned from the arbitrary zero at 2,000 atm, and V_0 is the volume of the specimen at 1 atm. Values of compression at pressures below 2,000 atm, therefore, appear as negative. The lowest pressure attained in these studies was 1,143 atm rather than 1,000 atm, and an additional measurement was made at 2,470 atm in most experiments, as shown in table 1. At the higher water contents it was not possible to attain the maximum pressure of 10,000 atm because of the excessive piston travel arising from the large transitions. In these experiments the initial readings were made at 9,000 atm. In experiments with 0.12 and 0.022 mole fractions of $\text{Ca}(\text{OH})_2$ attempts were made to attain 10,000 atm, but the immediate crystallization of ice-VI, initiated at a pressure of about 9,300 atm, produced too large a piston travel. In the measurement with 0.080 mole fraction of $\text{Ca}(\text{OH})_2$ the maximum pressure was only 9,100 atm and no ice-VI crystallized, but the measurement at 9,000 atm undoubtedly represents data for a metastable system.

The rather complex behavior of the tabular data is simplified by considering the compression-pressure curves shown in figures 1 and 2. Figure 1 contains the data for dry $\text{Ca}(\text{OH})_2$ and the mixtures of high $\text{Ca}(\text{OH})_2$ content, and corresponding data for water and the mixtures of low $\text{Ca}(\text{OH})_2$ content

¹ Figures in brackets indicate the literature references at the end of this paper.

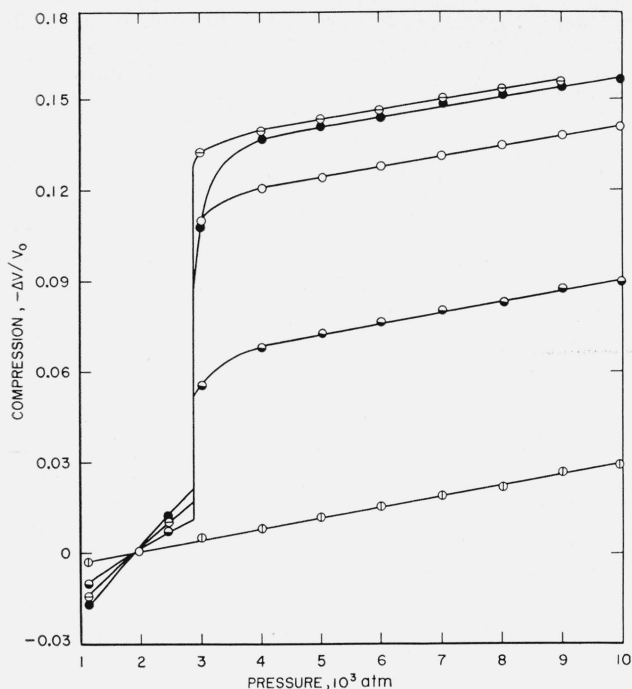


FIGURE 1. Compression of mixtures of Ca(OH)_2 and H_2O rich in Ca(OH)_2 .

○, 100 mole percent Ca(OH)_2 ; ●, 56 mole percent Ca(OH)_2 ; ○, 31 mole percent Ca(OH)_2 ; ●, 26 mole percent Ca(OH)_2 ; ○, 20 mole percent Ca(OH)_2 .

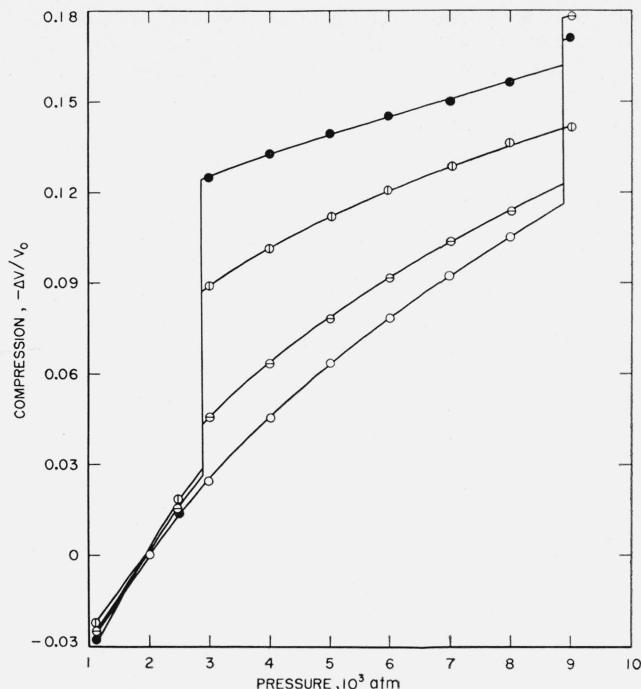


FIGURE 2. Compression of mixtures of Ca(OH)_2 and H_2O rich in H_2O .

●, 12 mole percent Ca(OH)_2 ; ○, 8 mole percent Ca(OH)_2 ; ○, 2.2 mole percent Ca(OH)_2 ; ○, 0 mole percent Ca(OH)_2 .

TABLE 1. Compression of Ca(OH)_2 - H_2O mixtures at 21°C

$-\Delta V/V_0$

Pressure	Mole fraction of Ca(OH)_2 in mixture							
	1	0.56	0.31	0.26	0.20	0.12	0.080	0.022
atm								
10,000	0.0296	0.0896	0.1411	0.1577				
9,000	.0266	.0869	.1385	.1547	0.1559	0.1708	0.1418	0.1778
8,000	.0217	.0830	.1350	.1517	.1528	.1564	.1362	.1139
7,000	.0189	.0799	.1314	.1483	.1502	.1500	.1287	.1035
6,000	.0150	.0762	.1281	.1440	.1467	.1451	.1207	.0917
5,000	.0113	.0723	.1245	.1411	.1433	.1394	.1120	.0786
4,000	.0073	.0678	.1206	.1366	.1390	.1328	.1018	.0633
3,000	.0048	.0554	.1097	.1080	.1323	.1248	.0891	.0459
2,470		.0070	.0115		.0111	.0144	.0175	.0155
2,000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
1,143	-.0037	-.0106	-.0149	-.0173	-.0174	-.0285	-.0218	-.0227

are given in figure 2. The data for liquid water were reported by Adams [4].

The following observations may be made from the curves of figures 1 and 2:

(1). The large discontinuity in volume in the system Ca(OH)_2 - H_2O involves both components because no comparable effect occurs in water or dry Ca(OH)_2 alone.

(2). Quantitatively, the amount of the discontinuity reaches a maximum for some intermediate composition of the mixture.

(3). No evidence exists for formation of ice-VI at low water contents, but at high water contents, ice-VI separates at approximately 8,800 atm in an

amount that increases with increasing water content.

(4). It may be concluded, therefore, that no liquid water is present at pressures above 3,000 atm in mixtures richer in Ca(OH)_2 than approximately 20 mole percent. This conclusion follows in part from observations (3) above and in part from the very low compressibilities (slopes of the $-\Delta V/V_0$ versus P curves) noted above 3,000 atm, which are characteristic of solid phases.

(5). In the presence of excess water, the discontinuity in volume at 2,800 atm is relatively sharp, but excess Ca(OH)_2 appears to "spread out" the discontinuity over a wider pressure range. Solid Ca(OH)_2 , therefore, appears to act as an impurity

and produces rounding of the corners of the discontinuity. As the phases present above 3,000 atm are believed to be all solids in mixtures rich in $\text{Ca}(\text{OH})_2$, contamination may be interpreted in terms of solid solutions.

(6). The compressibilities of the products formed above 2,800 atm in mixtures rich in $\text{Ca}(\text{OH})_2$ seem to be slightly less than the compressibility of the parent dry $\text{Ca}(\text{OH})_2$ (see table 2). It must be noted, however, that in this region two components are most probably present.

(7). The freezing pressure of water in mixtures rich in water is definitely below 9,000 atm. Inasmuch as pure water freezes under these conditions at approximately 8,800 atm [5], the material formed by the transition at 2,800 atm can be only sparingly soluble.

(8). The presence of excess water is clearly shown by the curvature noted above 3,000 atm in the curves of figure 2 and by the increasing resemblance of these curves to that for pure water as the water content increases. The strong dissimilarity between these curves above 3,000 atm and those of figure 1 is to be noted.

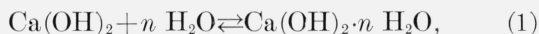
(9). The sharp drop in compressibility noticed on formation of the high-pressure phase in both figures 1 and 2 may be taken to indicate disappearance of water coincident with formation of the high-pressure phase.

TABLE 2. Volume discontinuity and compressibility data

Mole fraction of $\text{Ca}(\text{OH})_2$	Discontinuity in volume ($-\Delta V/V_0$) at 2,800 atm	Compressibility of high-pressure phase
1	cm^3/cm^3	atm^{-1}
0.56	0	3.7×10^{-6}
.31	0.0530	3.4
.26	.1012	3.3
.197	.1155	3.3
.120	.1172	3.3
.080	.0985	-----
.022	.0663	-----
0	.0182	-----
	0	-----

The compressibilities and discontinuities of volume referred to above are tabulated in table 2. These data were all obtained graphically and for this reason are not to be considered as precise. In addition, the evaluation of the discontinuity in volume is subject to obvious extrapolation errors incurred in extrapolating to 2,800 atm. The large curvature existing in the presence of excess water prevented graphical estimation of compressibilities for mixtures rich in H_2O .

As a result of the foregoing observations the reaction,



where n is an unspecified but fixed number, is believed to occur reversibly in the system $\text{Ca}(\text{OH})_2\text{-H}_2\text{O}$ at approximately 2,800 atm. The product of compression is written as a molecule containing

water of hydration merely for convenience as it is recognized that this material may be a form containing a complex aquo-cation [6]. As evidence against the former type of compound, it might be anticipated that a material containing ordinary water of crystallization would be less dense and probably more compressible than the parent anhydrous material. The possibility that the volume discontinuity arises from transformation of amorphous $\text{Ca}(\text{OH})_2$ to the more dense crystalline $\text{Ca}(\text{OH})_2$ is discounted because liquid water would not disappear in such a process and reversibility would not be expected.

The value of n in eq (1) may be bounded in the following manner: In these mixtures the quantity of product formed will be proportional to the quantity of the component present in deficiency. That is, in the presence of excess $\text{Ca}(\text{OH})_2$ the amount of reaction 1 will be determined by the quantity of water present, whereas in the presence of excess water the $\text{Ca}(\text{OH})_2$ becomes the determining factor. If the discontinuity in volume is taken to be a measure of the extent of reaction 1, a plot of mole fraction versus volume change at discontinuity should produce two lines intersecting at the composition corresponding to the pure compound. Such a graph of the data of table 2 is shown in figure 3. In figure 3, it is noted that in the region of excess H_2O good linearity is obtained but in the region of excess $\text{Ca}(\text{OH})_2$ curvature appears to exist. This may arise from interaction between the components in the presence of excess $\text{Ca}(\text{OH})_2$, as mentioned in observation (5). As a result of this curvature and the large slope of the linear section, it is not possible to place narrow limits on n . From figure 3 it would appear that it can be stated with assurance that $3 \leq n \leq 7$ and with considerable less certainty that $4 \leq n \leq 6$.

From the foregoing considerations, a rough phase diagram for the system $\text{Ca}(\text{OH})_2\text{-H}_2\text{O}$ at 21° can be constructed. This diagram is given in figure 4, and is based on the previous discussion. In the solution region, however, no measurements have been made, as it was believed that no conclusions could be

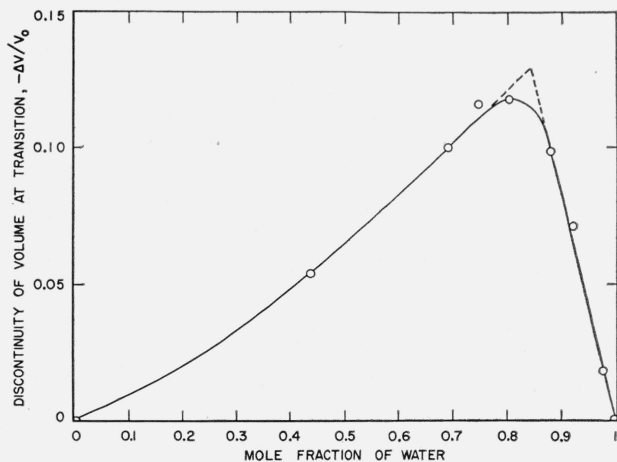


FIGURE 3. Effect of composition on discontinuity of volume at transition.

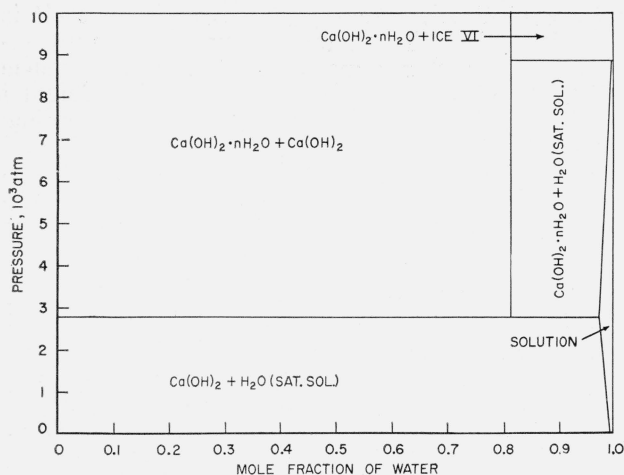


FIGURE 4. Proposed pressure-composition diagram for system $\text{Ca}(\text{OH})_2\text{-H}_2\text{O}$ at 21°C .

formed because of the slight solubility of $\text{Ca}(\text{OH})_2$. In this region, therefore, the course of the curve has been estimated. The initially increasing solubility of $\text{Ca}(\text{OH})_2$ with increasing pressure is inferred from the fact that its solubility increases with decreasing temperature [7]. Either this solubility decreases as is indicated at higher pressures or dissolved $\text{Ca}(\text{OH})_2$ is transformed into the compound of eq (1), which is sparingly soluble, since the saturated solution freezes at approximately the same pressure as pure H_2O . In the latter case, the transition line at 2,800 atm would extend across the solution region. Above 3,000 atm, the solid phase may be a mixture involving a solid solution. In the light of the present knowledge, satisfactory representation of any solid solution field is of dubious value. No attempt to include such a field on the diagram was made.

It must be emphasized that the data given here were obtained on decreasing the pressure, and figure 4 represents these findings. On increasing pressure, the low-pressure forms may persist at considerably higher pressures than those indicated in figure 4 for the transition lines. This feature is quite common in most high-pressure transitions.

The results reported here may be of significance geologically because hydrolyzable calcium salts in minerals subjected to pressures above 3,000 atm may tend to exist in the form of the high-pressure hydrate. This transition was originally observed in wet hydrated cement paste and in wet hydrated tricalcium silicate, both of which contain $\text{Ca}(\text{OH})_2$. However, it does not occur in gypsum-water mixtures at pressures as high as 10,000 atm. In view of the anomalous solubility behavior of calcium compounds and the large decrease in volume at the transition, however, there appears a distinct possibility of the occurrence of such processes at still higher pressures in the earth.

4. References

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